Graphene related materials for non-volatile resistive memories: a review

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In electronics, graphene is rapidly becoming the great hope for replacing and improving silicon semiconductors for future high performance devices. Since silicon semiconductors remain the basis of most commercial electronics (especially computing), the challenge for the next generation materials really becomes a great challenge. The graphene potentialities are attracting a lot of research funding, which in turn attracts researchers to probe opportunities in a number of directions such as novel graphene based transistors or spintronics. Another approach currently under development by some teams, is to employ graphene and other related nanomaterials to achieve non-volatile memories exploiting their "memresistive" behaviour. Indeed for e.g. computer high density storage memory, transistors work by storing an electrical charge. Thanks to "memresistive" materials we can store electrical resistance. That is, when a current is passed through these materials, their level of resistance to electricity (in Ohms) changes in a non-volatile and in an energetically "friendly" way. Resistive memory exploits the electric field responsive resistive switching of materials as an information write/erase principle for non-volatile data storage. The reading of resistance states is nondestructive, and the memory devices can be operated without transistors in every cell, thus making a cross-bar structure feasible. A large variety of solid-state materials have been found to show these resistive switching characteristics including solid electrolytes such as GeSe and Ag₂S, perovskites such as SrZrO₃, Pr_{0.7}Ca_{0.3}MnO₃, and BiFeO₃, binary transition metal oxides such as NiO, TiO₂, ZrO₂, and ZnO, organic materials, amorphous silicon (a-Si), and amorphous carbon (a-C). The main advantages of graphene related materials are not only that they seem to show extremely promising performances, but also that these materials provide more flexibility (physically) and potentially can lower the final cost of the devices, if scalable fabrication methods will be developed in parallel. Moreover we need only a two terminal device, which dramatically reduces the circuitry and allows the implementation of 3D architectures. Finally, this type of circuit commonly used for computer memory could be potentially easily printed or deposited (e.g. by spray-gun) on plastic sheets and used wherever flexibility is needed, such as in wearable electronics.

This contribution deals with the main scientific results and the potential market for graphene related materials in case of resistive non-volatile memories. Non-volatile memories are identified as key device for the future of computational system considering the reduced energy consumption compared to volatile-memories. However a specific new technology as not been identified up to now considering the issues related to scalability and cost. Graphene related materials offer an interesting and extremely promising alternative to existing technologies. In this contribution, we show the main works dealing with graphene layers, graphene-oxide and reduced graphene oxide. These works are quite recent but show impressing results especially in term of writing time and endurance/cyclability compared to common flash memories. The other main advantage of these materials is the potential of

developing a CMOS compatible technology highly scalable. Moreover the carbonaceous materials are easily available compared to rare earths and also compatible with flexible applications and can open new field of innovation.





SEM image of the device before (left panel) and after breakdown of the graphene layers (right panel). The arrows indicate the edges of the nanoscale gap [Stadley08].

Real crossbar memory devices based on Graphene Oxide on flexible substrate [Jeong10] [IEEE10].

Source	Material and configuration	On/Off max	Switching time	Cyclability	Retention time	Character	Energy consumption to write (J)
[Li08]	Graphitic layers on nanowire (planar)	10 ⁷	1µs	at less 1000 with no variation	1 day at less (15 days of consecutive switching)	Unipolar	~4 10 ⁻¹⁵
[Stadley08]	Graphene (planar)	10 ²	100ms	10 ⁵ without visible changes in signals	To be performed on more than 24 hours	Unipolar	Not clear
[Sinitski09]	Graphene (planar)	10 ⁷	1μs (tested limit)	at less 22000 with no variation	Not specified, even if the device is defined very stable	Unipolar	~8 10 ⁻¹⁷
	Carbon (vertical)	10 ⁶	1μs (tested limit)	at less 200	Not specified, even if the device is defined very stable	Unipolar	~7 10 ⁻¹⁷
[He09]	GO (vertical)	20	No data	at less 100	10 ⁴ seconds	Bi-polar	No switching time
[Jeong10]	GO (vertical)	10 ³	No data	at less 100	10 ⁵ seconds	Bi-polar	No switching time
[Hong11]	GO (vertical)	10 ³	No data	100 and failure	Not specified, even if the device is defined very stable	Bi-polar	No switching time
[Panin11]	GO (planar)	10 ³	No data	No data	No data	Bi-Polar and Uni-polar	No switching time
[Vasu11]	RGO (vertical)	10 ⁵	10µs	Few hundreds	Not specified, even if the device is defined very stable	Unipolar	~ 10 ⁻¹³

Table summarizing all the main characteristics of the main works on graphene based non-volatile memories